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Pyrolysis of biomass by thermal analysis–mass spectrometry (TA–MS)

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ABSTRACT

The kinetic parameters such as pre-exponential factor and activation energy of hemicellulose, cellulose, and lignin were well determined by the linear regressions of selected, sufficient thermogravimetric data, and close to literature values. The pyrolysis of biomass can be divided into four stages. There was only drying in the zeroth stage (<150 °C). In the first stage (150–250 °C), some light hydrocarbons were produced with the early pyrolysis of biomass. The biomass was mainly pyrolyzed in the second stage (250–500 °C) with higher reaction rates than those of other stages. The productions of H_2 and CO_2 in the third stage (>500 °C) may be able to be the evidence of self-gasification of char existing at higher temperatures.

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1. Introduction

Nowadays biomass has been commonly seen as an alternative and renewable energy source. By various conversion technologies (e.g., pyrolysis, gasification, torrefaction, etc.) of biomass, many kinds of bioenergy (biofuel) can be produced and used. Most of the biomass is composed of numerous components and thus has a heterogeneous property. In most cases, biomass is a mixture of hemicellulose, cellulose, lignin, ash, and minor amounts of other organics, which each pyrolyze or degrade at different rates and by different mechanisms and pathways (Bridgwater et al., 1999). Biomass is a term for all organic material that stems from plants including algae, trees, and crops (McKendry, 2002). Wood, crops, agricultural and forestry residues, and biodegradable components of municipal solid waste (MSW) and commercial and industrial wastes are some of the main renewable bioenergy resources available (Bridgwater, 2006). In Taiwan, there are a lot of sugarcanes, coffees, and bamboos planted or grown wildly, so residues of the plants are abundant. Thus this study primarily focused on these feedstocks and their experimental results.

In recent years, the authors have presented some results on microwave-induced pyrolysis of biomass, including properties of three-phase products (Huang et al., 2008), further investigation on gas product (Huang et al., 2010), and related outcomes. According to the authors' experience, it was hard to determine reaction kinetics and detailed mechanism of microwave-induced pyrolysis. This may be due to difficulties in real-time measuring of sample weight and product analysis, and disturbance caused microwave irradiation. However, perhaps the most critical limitation was from the existing apparatus of microwave-induced pyrolysis. The technology of thermogravimetric analysis (TGA) coupled with mass spectrometry (MS) is able to provide the reaction kinetics and products distribution of traditional pyrolysis, which may be capable of being regarded as a reference for newly developed pyrolysis technologies. There has been some literature concerning the thermal analysis–mass spectrometry (TA–MS) of volatile products from biomass (Varhegyi et al., 1988; Szabo et al., 1996; Worasuwannarak et al., 2007; Meszaros et al., 2007; Gomez et al., 2007; Barneto et al., 2009) and related materials (Materazzi, 1998; Otero et al., 2002; Li et al., 2003). According to the literature, one of the most attractive advantages of TA–MS is that it is able to afford the real-time and sensitive detection of evolved gases, which is an important and often a difficult task in many thermal applications.

Although the researches about the pyrolysis of biomass have been quite a lot, such as kinetics and product analysis, detailed studies on distribution of specific products with reaction temperature and time are relatively few. This study aimed to investigate the thermogravimetric property, reaction kinetics, and gas product distribution of pyrolysis of biomass by utilizing the TA–MS technology, and then to further discuss characteristics and novel discoveries in pyrolysis of biomass.

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2. Methods

2.1. Biomass

This study focused on the pyrolytic behaviour of five kinds of biomass feedstocks, such as coffee hulls, bamboo leaves, sugarcane bagasse, sugarcane peel, and filter paper (Advantec). The biomass feedstocks except filter paper were all agricultural and forest residues in Taiwan. Before being put into the TA–MS system, the biomass feedstock was air-dried, milled, and sieved (40 mesh) to yield powder samples. The proximate and the ultimate analyses of biomass feedstocks were in accordance with American Society for Testing and Materials (ASTM) Standard Test Method D 5142 and D 5291, respectively, and the results are listed in Table 1. Excluding bamboo leaves, the C/H/O ratios of biomass feedstocks were nearly the same as one another and analogous to that of the rice straw discussed in the authors' previous work (Huang et al., 2008). From this may be concluded that the biomass feedstocks have a close to common composition. In this article, the compositions and thermal properties of biomass feedstocks will be further discussed by means of the TA–MS analysis.

2.2. TA–MS experiment

TA–MS measurements were performed by a simultaneous thermal analyzer (Netzsch STA-409CD) coupled with a quadrupole mass spectrometer (Balzers QMA 400). In the interface between the two subunits, a skimmer coupling system was used to prevent the unnecessary condensation of evolved gases (i.e., tar production). The mass spectrometer was in the electron impact (EI) ionization mode at the electron energy of 70 eV and provided mass spectra up to 512 a.m.u. every 2 min. This study primarily discusses the mass spectra of 2, 15, 18, 27, 28, 30, 32, 44 a.m.u, which are assigned to represent H_2, CH_4, H_2O, C_2H_4, CO, C_2H_6, O_2, and CO_2, respectively. During the experiments, about 10 mg of sample (40 mesh sieved) was put in a ceramic crucible for each batch, and then heated in the TA–MS apparatus from room temperature to about 900 °C at the heating rate of 5 °C/min. In all experiments, the purge gas used was helium with a constant flow rate of 100 ml/min. Both the sensitivity of MS and the baseline of MS signals were checked by the measurement of 3 a.m.u., which can be seen as ^{3}He (the less abundant isotope of the purge gas used).

2.3. Reaction kinetics of pyrolysis of biomass

There have been so many researches on the kinetics of pyrolysis of biomass, and various mechanisms and assumptions have been illustrated. The rate of reaction for the decomposition of a solid depends on the temperature and the amount of substance (Orfao et al., 1999). Thus rate equation for the kinetics analysis can be expressed as:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{1}$$

where k is rate constant, $f(\alpha)$ represents a hypothetical model of reaction mechanism (Gil et al., 2010), and α is conversion ratio of biomass feedstock:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{2}$$

where m_0 is the initial mass of biomass sample, m_t is the mass at time t or temperature T, and m_f is the final mass at the end of pyrolysis. The rate constant can be derived from the Arrhenius equation:

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where A is pre-exponential factor, E_a is activation energy, R is the universal gas constant (8.314 J/k·mol), and T is temperature. Besides, the reaction model in Eq. (1) can be expressed as:

$$f(\alpha) = (1-\alpha)^n \tag{4}$$

where n is order of reaction. In many applications, the pyrolysis of biomass was assumed to be a first-order reaction (i.e., $n = 1$). Therefore, under a constant heating rate β (= dT/dt), Eq. (1) can be rearranged to:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (1-\alpha) \tag{5}$$

By the Coats–Redfern integral method (Coats and Redfern, 1964), Eq. (5) can be integrated to:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \tag{6}$$

For most values of activation energy and for the temperature range of pyrolysis, the term of $\ln[AR/\beta E_a(1{-}2RT/E_a)]$ can be regarded as a constant (Zhou et al., 2006). Thus a straight line may be obtained from a plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$. T is the average value of temperatures at which the thermogravimetric data best fit a straight line done by linear regression. From the linear regression of Eq. (6), the activation energy and the pre-exponential factor can be calculated by the slope and the intercept of the line, respectively.

3. Results and discussion

3.1. TGA results of biomass feedstocks

By means of the TA–MS experiments, TGA results of the biomass feedstocks can be obtained, as shown in Fig. S1 (see Supplementary data in the online version of this article). It can be seen that under the temperature up to about 900 °C, there was the most overall mass loss possessed by filter paper (88.74%), and bamboo

Table 1
The proximate and the ultimate analyses of biomass feedstocks.

	Proximate analysis (wt.%)[a,b]			Ultimate analysis (wt.%)[c]				
	VM	FC	Ash	C	H	N	S	O[d]
Coffee hulls	77.5	11.0	11.5	44.5	6.3	0.7	0.2	48.3
Bamboo leaves	70.3	18.7	11.0	40.5	5.8	0.7	0.2	52.8
Sugarcane bagasse	87.0	4.2	8.8	49.2	6.8	0.5	0.2	43.3
Sugarcane peel	77.3	10.1	12.6	44.0	6.5	0.8	0.3	48.4
Filter paper	89.0	9.2	1.8	45.1	6.2	0.8	0.2	47.7

[a] Dry basis.
[b] VM, volatile matter; FC, fixed carbon.
[c] Dry ash free basis.
[d] Calculated by difference.

leaves owned the least (61.15%). Meanwhile the overall mass losses of the other three biomass feedstocks were 75–82%. All the mass losses of the biomass feedstocks mainly occurred at the temperatures of 200–500 °C. The curves of mass versus temperature are clearly S-shaped except sugarcane bagasse. The mass profile of sugarcane bagasse demonstrated that unlike the other biomass feedstocks, there was an obvious mass change at the temperature of around 200 °C.

To further discuss the difference among the TGA results of the biomass feedstocks, derivative thermogravimetric (DTG) analysis was adopted. Combined diagrams presenting DTG results of the biomass feedstocks are shown in Fig. S2. Each of the DTG diagram shows only one peak excluding the diagram of sugarcane bagasse. Except the peak appearing at the temperature range coincident with the other feedstocks, there was also a smaller peak at the temperature of about 200 °C in the diagram of sugarcane bagasse. Several TGA results of the biomass feedstocks, such as accumulative mass losses (L_1, L_2, and L_3) at temperatures of less than 150 °C, 150–500 °C, and higher than 500 °C, respectively, total mass loss during TGA experiment (L_T), and mass-loss rate (R_P) and temperature (T_P) at the peak in the DTG diagram, respectively, are listed in Table 2.

As above mentioned, most of the biomass is primarily composed of hemicellulose, cellulose, and lignin. Refer to the study by Yang et al. (2007), the pyrolytic weight loss of hemicellulose, cellulose, and lignin mainly happened at the temperature ranges of 220–315 °C, 315–400 °C, and 160–900 °C, respectively. Besides, Idris et al. (2010) indicated that the moisture drying region in the pyrolysis oil palm biomass was at the temperature range of lee than 150 °C, and the pyrolytic degradation was mainly started from 180–200 °C till around 500 °C. Therefore, the overall mass loss was divided into three stages by temperature ranges of <150 °C, 150–500 °C, and >500 °C in this study. As shown in Table 2, the moisture contents of the biomass feedstocks that were assigned as the mass loss of the first stage (L_1) were only 0.11–3.42% of original feedstock weights. The second stage of mass loss is supposed to be in which the pyrolysis of biomass feedstock mainly occurred. The mass losses of the second stage (L_2) were 54.67–85.35% of original feedstock weights, so this means that 89.40–96.18% of the total mass losses (L_T) during the TGA experiments happened in the second stage. That the most part of the biomass reacted at the temperature range of 150–500 °C shall be recognized as the pyrolysis of its lignocellulose content. In this stage, both the hemicellulose and cellulose contents are able to completely decompose, but only part of the lignin can be reacted due to its low thermal reactivity.

The reactivity in the third stage was much less than that in the second stage. The mass losses of the third stage (L_3), which were only 2.73–5.38% of original feedstock weights, might come from the pyrolysis of lignin content, self-gasification, secondary reactions, or something unknown. The total mass losses (L_T) represent the entire reactivity of the biomass feedstocks under the TGA experiments. Bamboo leaves showed the least pyrolytic reactivity (61.15%), and filter paper performed the best (88.74%). This difference is highly coincident with that in the volatile matters of biomass feedstocks (Table 1). From this and the result of ultimate analysis are concluded, that the compositions of biomass feedstocks are different to some extent with one another.

Table 2
The TGA results of biomass feedstocks.

Biomass	L_1	L_2	L_3	L_T	R_P	T_P
	(%)				(%/min)	(°C)
Coffee hulls	0.96	73.28	4.14	78.38	5.01	340
Bamboo leaves	1.10	54.67	5.38	61.15	3.12	325
Sugarcane bagasse	3.42	76.13	2.92	82.47	2.81/4.14	205/335
Sugarcane peel	0.11	71.58	3.42	75.11	5.14	335
Filter paper	0.65	85.35	2.73	88.74	11.42	350

L_1, L_2, and L_3, accumulative mass loss at temperatures of <150 °C, 150–500 °C, and >500 °C, respectively; L_T, total mass loss during TGA experiment; R_P and T_P, mass-loss rate and temperature at the peak in the DTG diagram, respectively.

In Table 2, the mass-loss rate at the peak (R_P) in the DTG diagram also means the maximum mass-loss rate if there is only one peak. For coffee hulls, bamboo leaves, sugarcane peel, and filter paper, the maximum mass-loss rates by the TGA experiments were 5.01, 3.12, 5.14, and 11.42%/min, respectively. This difference was nearly coincident with that from the total mass losses of the biomass feedstocks discussed above. Moreover, compared to the other biomass feedstocks, the peak of filter paper was much higher and more concentrated at the temperature range of 300–400 °C, at which the cellulose pyrolyzed as indicated by Yang et al. (2007). According to this consistency, filter paper might be mainly composed of the cellulose, or at least, the TGA results of filter paper might be capable of representing some properties of the cellulose. The temperature at the peak (T_P) in Table 2 also means the corresponding temperature of maximum mass-loss rate, which were 340, 325, 335, and 350 °C for coffee hulls, bamboo leaves, sugarcane peel, and filter paper, respectively. The difference among the peak temperatures was not significant compared with that among the maximum mass-loss rates.

Except a negligible peak at the temperature of about 70 °C, there were two peaks in the DTG diagram of sugarcane bagasse, and the maximum mass-loss rates were 2.81% and 4.14%/min at the temperatures of 205 and 335 °C, respectively. Accumulative mass losses during the temperature ranges of the two peaks (170–230 and 295–380 °C) were about 18% and 32%, between which there was also an accumulative mass loss of around 20%. It seems that these mass losses under different temperature range might come from thermal decompositions of corresponding components in sugarcane bagasse. In addition to hemicellulose, cellulose, and lignin, major constituents of biomass also consist of organic extractives and inorganic minerals (Mohan et al., 2006). Thus the unique peak in the DTG diagram of sugarcane bagasse might be contributed by the constituent of less thermal-resistance part of hemicellulose or organic extractives. It is supposed that the formation and separation of peaks may come from several factors, such as the thermal reactivity and relative proportions of components, thermal efficiency, and the operating conditions of experiments (e.g., reaction atmosphere, temperature, heating rate, etc.).

3.2. Results of kinetics analysis

In the TGA result, several data (mass change by temperature or time) were selected to satisfy a best linear regression of Eq. (6). Their corresponding temperature range and results of kinetics analysis are listed in Table 3. All the regression results have nearly extreme coefficients of determination, R^2 (from 0.9949 to 1.0000). Therefore, the assumption that pyrolysis of biomass undergoes a first-order reaction should be proper. The pre-exponential factors differed with different biomass feedstocks and temperature ranges, and ranged from 6.33×10^{-2} to 2.30×10^{15} 1/s. Generally, the activation energy varied in the same manner and ranged from 22.68 to 210.78 kJ/mol. Although the temperature ranges selected are small, it is supposed that the linear regressions with R^2 as high as possible are able to prevent the disturbance of experimental errors (data noise) and provide the representative kinetic parameters at the corresponding temperature ranges. Since the composition of biomass is complicated, the kinetic parameters determined over a small temperature range may approach to those of a certain component. However, it is still believed that, as Vyazovkin and Wight (1998) pointed out, the capability of a mathematical model to

Table 3
The kinetic analysis of biomass pyrolysis.

Biomass	Temperature range (°C)	A (1/s)	E_a (kJ/mol)	R^2
Coffee hulls	195–220	6.33×10^{-2}	28.93	0.9949
	250–280	8.10×10^{3}	75.23	0.9998
	330–350	4.90×10^{5}	96.07	0.9991
Bamboo leaves	195–220	2.10×10^{-1}	31.41	0.9980
	245–280	5.85×10^{2}	62.74	0.9996
	310–330	1.17×10^{3}	66.29	1.0000
Sugarcane bagasse	190–210	1.64×10^{4}	67.65	0.9986
	250–305	1.08×10^{-1}	22.68	0.9998
	325–345	4.45×10^{3}	71.28	0.9981
Sugarcane peel	180–205	2.76×10^{1}	50.03	0.9990
	250–290	2.42×10^{2}	59.27	0.9998
	325–345	6.48×10^{5}	96.31	0.9983
Filter paper	255–275	2.58×10^{0}	48.14	0.9986
	300–320	2.28×10^{4}	88.38	0.9959
	340–360	2.30×10^{15}	210.78	0.9997

R^2: coefficient of determination.

produce meaningful information cannot be *only* characterized by the goodness of fit (italics added by the authors).

Most of the pre-exponential factors and the activation energy showed an increasing tendency with the increase in temperature. The kinetic parameters seem to show a kinetic compensation effect (KCE), which is a kind of interdependence between them. However, since no explanation has yet been generally agreed for the widespread occurrence of KCE relationships (Galwey, 2004), it will not be further discussed in this article. The positive correlation between the pre-exponential factor and the temperature may be due to that the pre-exponential factor is highly related with the temperature-dependent collision frequency described in the collision theory. In addition, parts of the components of biomass (e.g., hemicellulose) that can be pyrolyzed at lower temperature are supposed to have lower activation energy. Thus, there was also a positive correlation between the activation energy and the temperature. However, there was an exception for sugarcane bagasse. At the temperatures of 190–210 °C, both the pre-exponential factor and the activation energy were much higher than that at the temperatures of 250–305 °C. Furthermore, the pre-exponential factor at the temperatures of 190–210 °C was also higher than that at the temperatures of 325–345 °C. Compared with other biomass feedstocks, the pre-exponential factor of sugarcane bagasse at the temperatures of 190–210 °C was much higher and the activation energy of that was the highest. According to the DTG diagram of sugarcane bagasse, there was a peak of mass-loss rate at the temperature of around 200 °C. Unlike the DTG results of other biomass feedstocks that showed a composite outcome (i.e., thermal decompositions of multi-components) at lower temperatures, the unique peak of sugarcane bagasse may provide a message that there was a single reaction of a single component and/or with a single mechanism. Therefore, it seems that the extraordinary pre-exponential factor and activation energy may come from a thermal-decomposition reaction of some specific component in the sugarcane bagasse. If the specific component is assumed to be one or some kinds of hemicellulose, the kinetics parameters determined at temperatures of 190–210 °C may be able to represent the pyrolysis characteristics of hemicellulose, such as the pre-exponential factor of 1.64×10^4 1/s and the activation energy of 67.65 kJ/mol.

At the medium temperatures of 250–290 °C, the relatively low reactivity of coffee hulls, bamboo leaves, and sugarcane peel may come from composite reactions of multi-components. In other words, parts of the components of biomass such as hemicellulose, cellulose, and lignin were reacted at this temperature range. For the three biomass feedstocks pyrolyzed at the temperatures of 250–290 °C, the pre-exponential factor and activation energy were 2.42×10^2–8.10×10^3 1/s and 59.27–75.23 kJ/mol, respectively. However, at almost the same temperature range, the kinetics parameters of sugarcane bagasse and filter paper were much different from those of the other three biomass feedstocks. The pre-exponential factor and activation energy of the two were 0.108–2.58 1/s and 22.68–48.14 kJ/mol, respectively. The kinetics parameters of coffee hulls, bamboo leaves, and sugarcane peel shall be due to the composite reactions of multi-components. However, the kinetics parameters of sugarcane bagasse and filter paper were relatively small and, therefore, may be capable of being regarded as the thermal properties of a single material (e.g., the lignin).

As mentioned above, there was a very high peak at the temperature of about 350 °C in the DTG diagram of filter paper, and then this peak may be able to represent the pyrolytic result of cellulose. During the peak period at the temperatures of 295–385 °C, the mass loss was sum up into about 77%. If the ratios of the mass loss after 385 °C and the residue after TGA experiment are both further excluded, the accumulative mass loss during the peak period will be turned into around 94%. This high percentage provides an additional proof that the filter paper should be primarily composed of a kind of material which can be highly supposed to be cellulose. Therefore, from the kinetics analysis of filter paper, both the pre-exponential factor of 2.30×10^{15} 1/s and the activation energy of 210.78 kJ/mol are supposed to be close to pyrolysis characteristics of cellulose.

According to the kinetics analyses of the biomass feedstocks discussed above, there were the pre-exponential factors and the activation energy of hemicellulose, cellulose, and lignin concluded by some evidences and assumptions, as listed in Table 4. Most of the pre-exponential factors and the activation energy calculated by the present study do not differ much from the literatures (Varhegyi et al., 1997; Rao and Sharma, 1998; Gronli et al., 1999; Orfao et al., 1999; Vamvuka et al., 2003; Yang et al., 2004) that all discussed the pyrolysis of lignocellulosic materials via first-order reaction kinetics. However, some of the literature used different integral methods with one another. These small disagreements may reflect in part simple differences in samples or result from unidentified, systematic temperature measurement errors that are accentuated at high heating rates (Antal et al., 1998). Xylan has been used by some researches (Varhegyi et al., 1997; Rao and

Table 4
The first-order reaction parameters of biomass pyrolysis.

Lignocellulose literature (sample)	β (°C/min)	A (1/s)	E_a (kJ/mol)
Hemicellulose			
Rao and Sharma (1998) (xylan)	20	1.93×10^{9}	105.0
Vamvuka et al. (2003) (straw)	10	2.08×10^{9}	120.8
Yang et al. (2004) (xylan)	10	2.09×10^{3}	69.39
Present study (bagasse)	5	1.64×10^{4}	67.65
Cellulose			
Varhegyi et al. (1997) (cellulose)	10	3.16×10^{18}	240
Rao and Sharma (1998) (cellulose)	20	4.69×10^{5}	82.7
Gronli et al. (1999) (cellulose)	5	1.0×10^{19}	244
Orfao et al. (1999) (cellulose)	5	1.14×10^{15}	210
Vamvuka et al. (2003) (straw)	10	2.13×10^{18}	231.8
Yang et al. (2004) (cellulose)	10	5.6×10^{16}	227.02
Present study (filter paper)	5	2.30×10^{15}	210.78
Lignin			
Varhegyi et al. (1997) (lignin)	10	$10^{0.3}$–10^{3}	34–65
Rao and Sharma (1998) (lignin)	20	5.39×10^{4}	67.0
Vamvuka et al. (2003) (straw)	10	5.90×10^{-1}	31.0
Yang et al. (2004) (lignin)	10	4.91×10^{-5}	7.80
Present study (bagasse/filter paper)	5	1.34×10^{0}	35.41

β, heating rate; A, pre-exponential factor; E_a, activation energy.

Sharma, 1998; Orfao et al., 1999; Yang et al., 2004) to represent the pyrolytic behaviour of hemicellulose. This can be due to the difficulty to obtain commercial hemicellulose (Yang et al., 2004). Orfao et al. (1999) had mentioned that the thermal decomposition of xylan and lignin can not be described by first-order reaction kinetics. However, in this study, the kinetics parameters of hemicellulose and lignin can be well determined by the assumption that the pyrolysis of biomass feedstock accords with first-order reaction. This may be due to that by selecting part of the thermogravimetric data (at least five) that provided the best result of linear regression, an almost straight line can be achieved and its slope and intercept can be further calculated to obtain the kinetics parameters, the activation energy and the pre-exponential factor. The thermal properties of lingocellulose (especially lignin) may change during the pyrolysis due to their complicated compositions. Too many data may result in poor result of linear regression that comes from a composite effect of multi-components. Therefore, thermogravimetric data over a small interval of temperature or time can provide a good linear regression in the kinetics analysis as illustrated in this study, in spite of which method of integration or other calculation applied.

3.3. Gas product analysis

By means of TA–MS analysis, thermogravimetric data can be obtained as well as information about the product distribution. This study primarily focused on the production of permanent gases such as H_2, CO, CO_2, and O_2, some light hydrocarbons including CH_4, C_2H_4, and C_2H_6, and H_2O. In the result of mass spectrometry, the atomic mass units (a.m.u.) of 2, 28, 44, 32, 30, and 18 represented H_2, CO, CO_2, O_2, C_2H_6, and H_2O, respectively, with respective to the molecular weights of the gas compounds. The a.m.u. of 15 and 27 instead of 16 and 28 were selected to represent CH_4 and C_2H_4, respectively, for the purpose of preventing the interference from other atoms or molecules that have the same atomic or molecular weights, since both the two compounds can easily release a hydrogen atom in the electric field of mass spectrometer. Besides, although the a.m.u. of 30 and 32 can be regarded as methanal (CH_2O) and methanol (CH_3OH) as well, they generally have the highest relative abundance at the a.m.u. of 29 and 31 in the mass spectra, respectively. Not like this, C_2H_6 and O_2 have the highest relative abundance at the a.m.u. of 30 and 32 in the mass spectra where the abundances at the other a.m.u. are quite low. Therefore, it is supposed to be appropriate to regard the a.m.u. of 30 and 32 as representatives of C_2H_6 and O_2, respectively. Parenthetically, this study has referred to the database of National Institute of Standards and Technology (NIST) for the help of a.m.u. selection. However, since there is still a possibility that the signal at an a.m.u. may come from the contributions of various atoms or molecules, the interference among them (e.g., accumulated signals) is supposed to be inevitable.

A signal of ion current can be seen as the existence of a compound, or an atom that was generated by the electron-impact ionization of the mass spectrometry. Therefore, the product analysis can be achieved with observations on ion-current changes in TA–MS results. When a peak is formed in the ion-current profile, a corresponding product can be quantitatively determined by integrating the peak. Combined diagrams of the ion-current profiles versus temperatures of coffee hulls, bamboo leaves, sugarcane bagasse, sugarcane peel, and filter paper are shown in Fig. 1. It can be clearly seen that for all the biomass feedstocks, most of the gas products were primarily generated at the same temperature range of 250–500 °C. However, H_2 was produced much more at higher temperatures (>500 °C). Peaks at lower temperatures (<150 °C) expressed the drying of biomass feedstocks. In the TA–MS diagram of sugarcane bagasse, there were some peaks at the temperature of about 200 °C, which was coincident with the peak in the DTG diagram. Qualitative analyses can be easily achieved by interpreting the TA–MS results, but there was lack of quantitative analysis of mass spectrometry. To further discuss the magnitude and distribution of the gas products, a semi-quantitative analysis was applied and can be accomplished by the integration of the ion-current peak, as shown in Table 5. According to the temperatures that the gas products appeared, the overall temperature range that the TA–MS proceeded was divided into four stages, such as the zeroth, the first, the second, and the third stage, by the temperatures of <150 °C, 150–250 °C, 250–500 °C, and >500 °C, respectively.

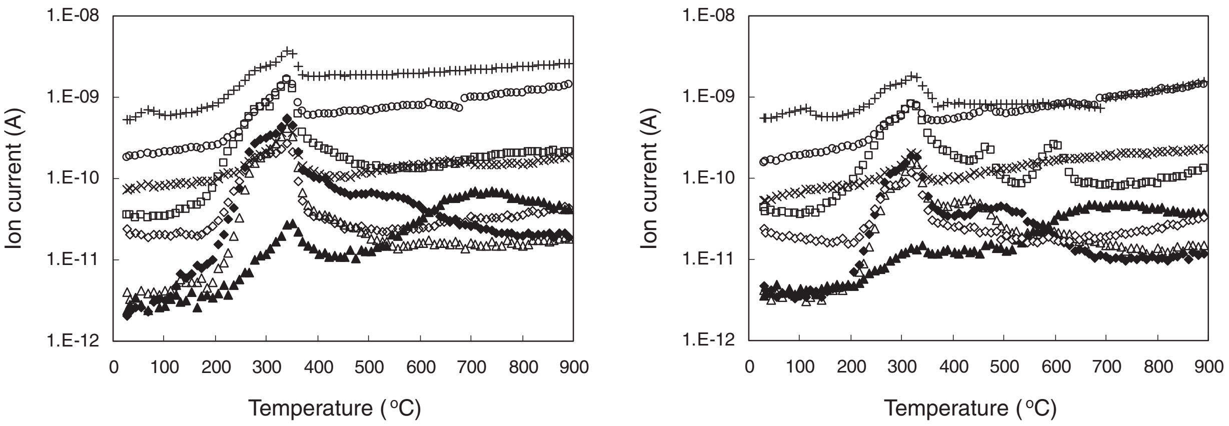
Firstly, in the zeroth stage (<150 °C), there was only H_2O detected in the spectrums of the biomass feedstocks except filter paper. Thus it can be thought that there was no moisture content in the filter paper. Besides, since no gas product but H_2O was found in this stage, it can be supposed that there was no pyrolysis of biomass at that time (temperature). Therefore, it was named the zeroth stage with respect to the existence of the pyrolysis or none. Secondly, the gases such as CH_4, C_2H_4, C_2H_6, and H_2O were produced by the pyrolysis of sugarcane bagasse in the first stage (150–250 °C), where no obvious gas can be produced by the pyrolysis of other biomass feedstocks. Unlike these light hydrocarbons and H_2O, the permanent gases including H_2, CO, CO_2, and O_2 were not found in the first stage of the pyrolysis of sugarcane bagasse. This may imply that the earlier productions (compared to those in the second stage) of the light hydrocarbons and H_2O are highly related to the pyrolysis of hemicellulose that has been discussed above. Otherwise, there may be something different between the contents of sugarcane bagasse and the other biomass feedstocks.

Thirdly, most of the gas products except H_2 were produced in the second stage (250–500 °C). It can be regarded as that the pyrolysis of the biomass feedstocks mainly happened in this stage. In Fig. 1, both the peaks of H_2 and CO are narrower than those of the other gas products, especially CH_4 and CO_2. This phenomenon was even clearer in the product distribution of filter paper. Since the filter paper can be seen as a representative of cellulose as mentioned above, it may be supposed that compared with hemicellulose and lignin, the pyrolysis of cellulose can produce more both of H_2 and CO, or at least they are highly related. To discuss the relationship between the gas production and the reactivity of biomass feedstock, the Pearson product-moment correlation coefficient (r) was used:

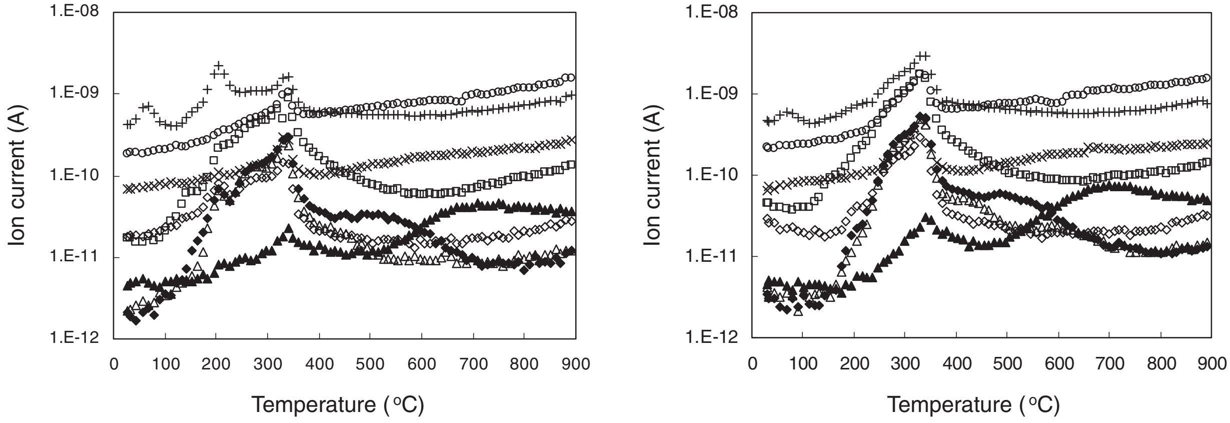
$$r(x,y) = \frac{\sum(x-\bar{x})(y-\bar{y})}{\sqrt{\sum(x-\bar{x})^2\sum(y-\bar{y})^2}} \tag{7}$$

where x and y are two data sets, and the top lines represent their means. The relationship was evaluated by calculating the correlation coefficients between the integral areas of ion-current peaks of gas products and the accumulative conversion ratios of biomass feedstocks at the temperatures of 300–350 °C, as listed in Table 6.

The temperature range was selected for the purpose that to collect the conversion data of the biomass feedstocks at the same period where they were all highly reacted. Thus at this temperature range, the production of H_2 was in very strong correlation ($r = 0.9989$) with the reactivity of biomass, and the productions of CO and CH_4 were in strong ones ($r = 0.8707$ and 0.8233, respectively). On the contrary, the productions of O_2 and H_2O were almost not related to the reactivity of biomass with the correlation coefficients of 0.0670 and 0.0321, respectively. The productions of the other gases showed moderate correlations with the reactivity of biomass. Since the cellulose is supposed to undergo pyrolysis at the temperature range including 300–350 °C where all the biomass feedstocks were reacted the most, the result of correlation analysis may provide another proof that the productions of H_2


(a) Coffee hulls

(b) Bamboo leaves


(c) Sugarcane bagasse

(d) Sugarcane peel

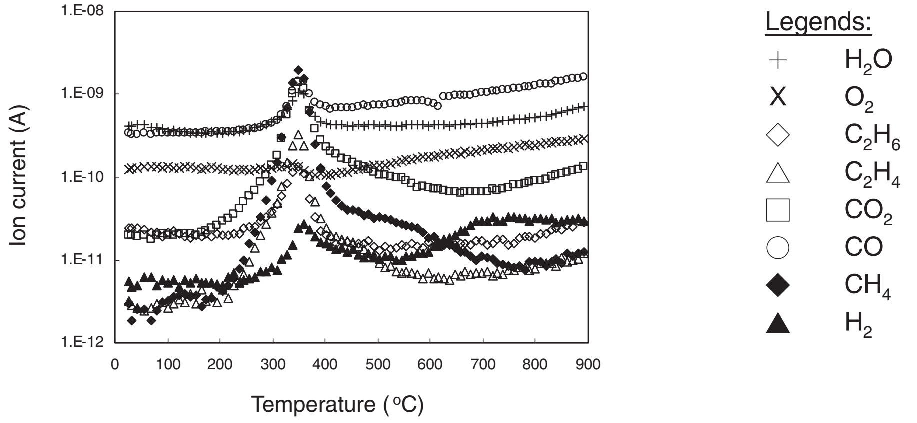

(e) Filter paper

Fig. 1. The TA–MS analyses of biomass feedstocks.

and CO are highly related to the cellulosic content in the biomass as above mentioned. Otherwise, at the temperatures of 400–500 °C, there were CO, CO_2, and C_2H_4 as well produced by the pyrolysis of bamboo leaves, but their quantities were quite small.

At the temperatures more than 500 °C (the third stage), there was less biomass pyrolysis and almost no gas production except CO_2 for the bamboo leaves and H_2 for all the biomass feedstocks. The unusual CO_2 production had a maximum rate at the temperature of 597 °C and started at about 550 °C that H_2 was also going to be produced for the second time. Therefore, maybe there is some kind of relationship between the productions of CO_2 and H_2 at higher temperatures. For all the biomass feedstocks except filter paper, the productions of H_2 in the third stage were much higher than those in the second stage (about 4–12 times). The quantities of H_2 produced by the pyrolysis of filter paper were almost the same in both stages. In the third stage, there was a maximum rate of H_2 production at the temperature about 700 °C. Bamboo leaves met the maximum rate earliest (668 °C) and sugarcane bagasse

Table 5
The product analysis by TA–MS.

Gas	Stage	Logarithmic ion current@temperature of peak (°C)				
		Coffee hulls	Bamboo leaves	Sugarcane bagasse	Sugarcane peel	Filter paper
H_2	2nd	−10.14@350	−10.60@340	−10.42@340	−10.15@340	−10.00@360
	3rd	−9.35@709	−9.52@668	−9.56@749	−9.57@700	−9.96@718
CO	2nd	−8.37@340	−8.64@319 −9.33@474	−8.76@340	−8.35@330	−8.34@349
CO_2	2nd	−8.15@340	−8.27@319 −9.63@464	−8.16@340	−8.07@330	−8.16@349
	3rd		−9.12@597			
CH_4	1st			−10.09@205		
	2nd	−8.58@340	−8.93@319	−8.80@340	−8.68@330	−8.04@349
C_2H_4	1st			−9.17@205		
	2nd	−7.59@340	−8.18@319 −9.07@433	−7.90@329	−7.57@330	−7.92@349
C_2H_6	1st			−9.05@205		
	2nd	−7.71@340	−8.23@319	−8.20@329	−7.75@330	−8.29@349
O_2	2nd	−7.70@340	−8.33@319	−8.09@329	−7.78@330	−8.95@339
H_2O	0th	−8.25@68	−8.09@112	−8.02@ 68	−8.29@ 68	
	1st			−7.32@205		
	2nd	−6.85@340	−7.07@319	−7.63@340	−6.89@330	−7.51@349

Table 6
The relationships between the reactivity of biomass and the productions of different gases in the second stage.

Gas	Correlation coefficient, *r*	Correlation
H_2	0.9989	Very strong
CO	0.8707	Strong
CO_2	0.5436	Moderate
CH_4	0.8233	Strong
C_2H_4	0.4451	Moderate
C_2H_6	0.2593	Weak
O_2	0.0670	Very weak
H_2O	0.0321	Very weak

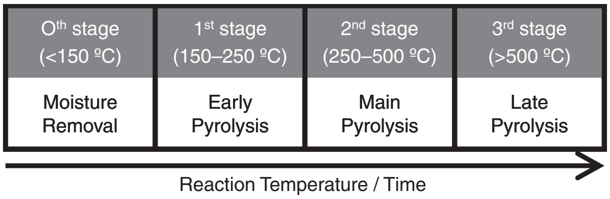


Fig. 2. The four stages in pyrolysis of biomass.

the latest (749 °C). Referring to the low reactivities of the biomass feedstocks at higher temperatures, the second production of H_2 was too high to be ignored. This may provide evidence of some kind of secondary reaction, such as self-gasification or the others. The integral areas of ion-current peaks of H_2 produced in the third stage were highly correlated with the conversion ratios of biomass feedstocks happened at the temperatures of 500–700 °C ($r = 0.7790$) and the integral areas of ion-current peaks of O_2 and H_2O produced in the second stage ($r = 0.7905$ and 0.7027, respectively). Thus the H_2O and the char (represented as C) both generated in the second stage may interact as:

$$C + H_2O \rightarrow CO + H_2 \tag{8}$$

which is the gasification of char with steam. However, CO was not found in the third stage for all the biomass feedstocks. To take the production of CO_2 from bamboo leaves at higher temperatures into account, there maybe exist a pathway that sink the CO by Eq. (8):

$$CO + 0.5O_2 \rightarrow CO_2 \tag{9}$$

where O_2 can be obtained from the production in the second stage that is also highly correlated with the H_2 production in the third stage. Then there is a new equation by combining Eqs. (8) and (9):

$$C + H_2O + 0.5O_2 \rightarrow CO_2 + H_2 \tag{10}$$

Therefore, Eq. (10) may be capable of representing the self-gasification of biomass at higher temperatures. There are only a few literatures that discussed the self-gasification in the pyrolysis of biomass. Menendez et al. (2007) and Dominguez et al. (2008) pointed out a self-gasification of char by CO_2 that is produced during microwave pyrolysis. Tian et al. (2007) mentioned a self-gasification of cane trash by H_2O as moisture in the trash or pyrolytic H_2O. On the other hand, Gomez et al. (2007) and Barneto et al. (2009) regarded H_2, CH_4, CO, and CO_2 at higher temperatures (above about 500 °C) as the products of charring process, where H_2O should be generated as well. In this study, the ion current of H_2O remained nearly constant at the higher temperatures. This may be attributed to an offset of self-gasification and charring processes. Although this study has presented the evidence of self-gasification by the TA–MS results, further investigations are still needed to prove this phenomenon.

3.4. Four stages in pyrolysis of biomass

According to the TA–MS results and relevant discussion mentioned above, the pyrolysis of biomass can be divided into four stages, as shown in Fig. 2. In the zeroth stage, there is no reaction of pyrolysis but moisture removal due to the low temperature (<150 °C). Once the temperature is high enough (150–250 °C), part of the biomass (like hemicellulose) can be thermally decomposed at lower reaction rate. This is the first stage in pyrolysis of biomass to produce light hydrocarbons. In the second stage (250–500 °C), the most part of the biomass (hemicellulose and cellulose) can be rapidly pyrolyzed, and most of the gas products will be produced then. At higher temperatures (>500 °C), only a little part of the biomass which should be the unreacted lignin, still undergoes pyrolysis. The productions of H_2 and CO_2 in the third stage may prove the possibility of self-gasification of biomass or, more precisely, residual char generated in earlier stages.

4. Conclusions

The properties and characteristics of pyrolysis of biomass were researched by thermal analysis–mass spectrometry (TA–MS). The kinetics parameters of lignocelluloses determined by thermogravimetric data were close to literature values. The pyrolysis of biomass can be divided into four stages. Only water and light hydrocarbons were detected in the zeroth and the first stage, respectively. Most of the gas products were generated in the second stage, after which there was no production of gas except H_2 and CO_2. The gases found in the third stage may provide the evidence of self-gasification of char existing at higher temperatures.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2010.11.049.

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